

The preparation, characterisation and electronic structures of 2,4-pentadiynynitrile (cyanobutadiynyl) complexes†

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Convenient preparative routes to mononuclear ruthenium complexes containing the 2,4-pentadiynynitrile, or cyanobutadiynyl, ligand are described. The electronic properties of the $[\text{C}_5\text{N}]^-$ ligand are closely related to those of not only the cyanide ($[\text{CN}]^-$) and 2-propynynitrile or cyanoacetylide ($[\text{C}\equiv\text{CC}\equiv\text{N}]^-$) ligands, but also those of the isoelectronic polyynyl ($[\{\text{C}\equiv\text{C}\}_n\text{R}]^-$) ligands.

The unsaturated cyanocarbon 2,4-pentadiynenitrile (cyano-butadiyne, $\text{HC}\equiv\text{CC}\equiv\text{CC}\equiv\text{N}$, **1**) and other similarly structured cyanocarbons are thought to occur within interstellar clouds, the circumstellar environment of carbon-rich stars and within the atmosphere of Titan.¹ Although recent synthetic developments have permitted the isolation of tens of milligram quantities of pure **1**,² sufficient for improved spectroscopic investigations,³ the use of **1** directly in subsequent synthetic work is still extremely limited.⁴ Nevertheless, the 2,4-pentadiynynitrile anion $[\text{C}\equiv\text{CC}\equiv\text{CC}\equiv\text{N}]^-$ is an attractive formal synthetic target that would extend the homologous series of cyanide ($[\text{CN}]^-$)⁵ and cyanoacetylide ($[\text{C}\equiv\text{CC}\equiv\text{N}]^-$)⁶ ligands, and complement the larger and isoelectronic families of polyynyl ($[\{\text{C}\equiv\text{C}\}_n\text{R}]^-$) and polyynediyl ($[\{\text{C}\equiv\text{C}\}_n]^{2-}$) ligands.⁷

We have recently described convenient methods for the synthesis of metal complexes $\text{M}(\text{C}\equiv\text{CC}\equiv\text{N})\text{L}_n$ ($\text{ML}_n = \text{Fe}(\text{dppe})\text{Cp}$,⁸ $\text{Ru}(\text{PPh}_3)_2\text{Cp}$,⁹ $\text{Ru}(\text{dppe})\text{Cp}^{*10}$) containing the 2-propynynitrile (cyanoacetylide) ligand from reactions of phenylcyanate,

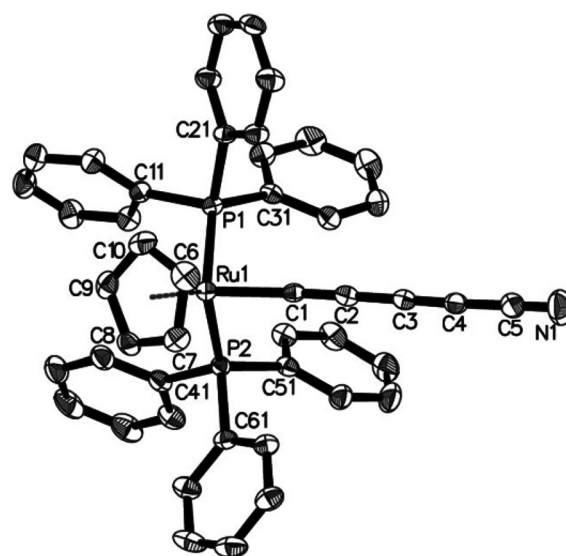


Fig. 1 A plot of a molecule of **4a**. Selected bond lengths (Å) and angles (°): Ru1–C1 1.958(3); C1–C2 1.230(4); C2–C3 1.346(5); C3–C4 1.215(5); C4–C5 1.362(5); C5–N1 1.148(5); Ru1–P1 2.2947(8); Ru1–P2 2.3050(9); Ru1–C1–C2 171.9(3); C1–C2–C3 178.9(4); C2–C3–C4 178.7(4); C3–C4–C5 176.6(4); C4–C5–N1 179.8(5).

PhOCN , with a metal alkynyl anion^{8,9,10a} or 1-cyano-4-dimethylamino pyridinium tetrafluoroborate ($[\text{CAP}]\text{BF}_4$) with an alkynyl complex, the latter proceeding through an intermediate cyano-vinylidene.^{10b} In a useful refinement to these published procedures, we have found that $\text{Ru}(\text{C}\equiv\text{CC}\equiv\text{N})(\text{PPh}_3)_2\text{Cp}$ (**3a**) and $\text{Ru}(\text{C}\equiv\text{CC}\equiv\text{N})(\text{dppe})\text{Cp}^*$ (**3b**) can be prepared in one-pot reactions from the very easily obtained vinylidenes $[\text{Ru}(\text{C}=\text{CH}_2)(\text{L}_2)\text{Cp}]\text{PF}_6$ with KO^tBu and $[\text{CAP}]\text{BF}_4$.†

The synthesis of complexes featuring the cyanoacetylide ligand has prompted us to consider compounds containing the next member of this family of unsaturated cyanocarbon ligands, 2,4-pentadiynynitrile. Reaction of $\text{Ru}(\text{C}\equiv\text{CC}\equiv\text{CCSiMe}_3)(\text{PPh}_3)_2\text{Cp}^{11}$ with $[\text{CAP}]\text{BF}_4$ ¹² in CH_2Cl_2 at room temperature gave the desired 2,4-pentadiynynitrile

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†Electronic supplementary information (ESI) available: Full synthetic details, spectroscopic characterisation, electrochemical data and computational details. Plots of **4a** and **4b** and tables of crystallographic details, bond lengths and angles. Plots of selected frontier orbitals, tables of orbital energies, Mulliken population analyses and Cartesian coordinates from $[\text{2a}'\text{--}4\text{a}']^{n+}$ ($n = 0, 1$). CCDC 916018 and 916019. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c3dt33052d

complex $\text{Ru}(\text{C}\equiv\text{CC}\equiv\text{CC}\equiv\text{N})(\text{PPh}_3)_2\text{Cp}$ (**4a**) in 44% isolated yield after chromatographic purification and crystallisation.[†]

The isomeric 2-ethynyl-cyanovinylidene, $[\text{Ru}\{\text{C}=\text{C}(\text{C}\equiv\text{CR})-(\text{CN})\}(\text{PPh}_3)_2\text{Cp}]^+$, which could be formed by addition of cyanogen to the C_β carbon of the diyne reagent, was not observed. The ligand structure was established by resonances in the ^{13}C NMR spectrum at 145.5 (t, $J_{\text{CP}} = 26$ Hz, C_α), 93.4 (br, C_β), 72.4 (C_γ), 53.4 (C_δ) and 108.4 (C_ϵ), and $\nu(\text{C}\equiv\text{CC}\equiv\text{CC}\equiv\text{N})$ bands at 1977w, 2112m, 2192w cm^{-1} in the IR spectrum, and a single crystal X-ray diffraction study (Fig. 1).[†] The closely related complex $\text{Ru}(\text{C}\equiv\text{CC}\equiv\text{CC}\equiv\text{N})(\text{dppe})\text{Cp}^*$ (**4b**) was prepared in an entirely analogous fashion, albeit in substantially lower yield (10%) after crystallisation.[†]

The homologous series $\text{Ru}(\text{C}\equiv\text{N})(\text{L}_2)\text{Cp}'$ (**2**),^{10,13} $\text{Ru}(\text{C}\equiv\text{CC}\equiv\text{N})(\text{L}_2)\text{Cp}'$ (**3**)^{9,10} and $\text{Ru}(\text{C}\equiv\text{CC}\equiv\text{CC}\equiv\text{N})(\text{L}_2)\text{Cp}'$ (**4**) [**a**: $(\text{L}_2)\text{Cp}' = (\text{PPh}_3)_2\text{Cp}$; **b**: $(\text{L}_2)\text{Cp}' = (\text{dppe})\text{Cp}^*$] permits a detailed investigation of the characteristics of these cyanocarbon ligands.¹⁴ The key metric parameters of the $\text{Ru}-\text{C}\equiv\text{CC}\equiv\text{CC}\equiv\text{N}$ chain in **4a** and **4b** are essentially independent of the nature of the auxiliary ligands within the limits of precision. Nevertheless, the alternation in the bond lengths along the chain clearly supports description of the C_5N ligand in terms of a 2,4-pentadiynynitrile moiety. Structural comparisons across the series **2**, **3** and **4** are most readily made within the $\text{Ru}(\text{dppe})\text{Cp}^*$ series, with the structures of **2b** and **3b** having been reported earlier.^{10a} The $\text{Ru}-\text{C}(1)$ bond lengths in **3b** and **4b** are shorter than in the cyano derivative **2b**, and also shorter than in alkynyl and diyne complexes $\text{Ru}(\text{C}\equiv\text{CH})(\text{dppe})\text{Cp}^*$ (2.015(2) Å)¹⁵ and $\text{Ru}(\text{C}\equiv\text{CC}\equiv\text{CH})(\text{dppe})\text{Cp}^*$ (2.015(4) Å).¹¹ The elongation of the average $\text{Ru}-\text{P}$ bond length on moving from **3b** to **4b** is consistent with trends observed in related polyyne series and reflects decreasing $\text{C} \rightarrow \text{Ru}$ σ -donation, rather than any pronounced increase in the $\text{Ru} \rightarrow \text{C}_n\text{N}$ π -back-bonding.^{10b,14,16} The seven atom $\text{RuC}\equiv\text{CC}\equiv\text{CC}\equiv\text{N}$ chain in **4a** is linear, with individual angles along the chain varying between 176.6–179.8°. In contrast the RuC_5N chain in **4b** is substantially bowed, likely a consequence of packing effects,[†] with individual angles falling between 166.1–178.1°.¹⁷

There has been considerable interest in the development of synthetic routes to metal complexes containing polyyne ($\{\text{C}\equiv\text{C}\}_n\text{R}\}$ ligands, and in the molecular and electronic structures of these long carbon-strings.^{7,14,17} The cyanocarbon ligands contained in **2–4** are isoelectronic with ethynyl ($[\text{C}\equiv\text{CH}]^-$), 1,3-butadiynyl ($[\text{C}\equiv\text{CC}\equiv\text{CH}]^-$) and 1,3,5-hexatriynyl ($[\text{C}\equiv\text{CC}\equiv\text{CC}\equiv\text{CH}]^-$) moieties. When this isoelectronic analogy is considered alongside the simple synthetic routes available for **2–4**, and the almost ubiquitous nature of the cyanide ligand in inorganic chemistry,⁵ the cyanocarbon complexes make a clear case for further investigation.

Electronic structure calculations (BLYP35/def2-SVP/COSMO)[†] have been undertaken on the representative series **2a'–4a'** (the prime notation being used to indicate the computational systems), which complement earlier DFT studies.¹⁴ The optimised structures were in good agreement with the available crystallographic data, with $\text{Ru}-\text{C}(1)$ bond lengths

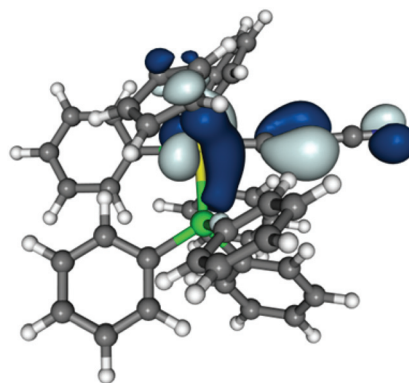


Fig. 2 Isosurface plot (± 0.04 (e bohr $^{-3}$) $^{1/2}$) of the HOMO of **3a'**.

decreasing with increasing chain length, and bond length alternation clearly apparent in the cyanocarbon ligand. The calculated $\nu(\text{C}_n\text{N})$ vibrational frequencies are in fairly good agreement with experimental values in condensed phases (**2a'** 2131 cm^{-1} , **2a** 2070 cm^{-1} ; **3a'** 2039, 2248 cm^{-1} , **3a** 2000, 2180 cm^{-1} ; **4a'** 1998, 2144, 2259 cm^{-1} , **4a** 1977, 2112, 2192 cm^{-1}).

The character and distribution of the frontier orbitals over the RuC_nN chain is sensitive to the nature of the cyanocarbon fragment. In the case of the parent cyano complex **2a'** the HOMO is essentially metal centred (55%), with only a small contribution from the cyano ligand (4%), whilst the HOMO–1, which lies only 0.1 eV lower in energy, has modestly more mixed $\text{Ru d}/\text{CN } \pi$ -character (52/14%; Fig. S1[†]). The LUMO also has appreciable metal character, and is of δ -symmetry with respect to the $\text{CN } \pi$ -systems.

The general characteristics of these orbitals are preserved in **3a'** although the ordering of the metal d- and $d\pi$ -orbitals are reversed, with the HOMO now being extensively delocalised over the five atom $\text{RuC}\equiv\text{CC}\equiv\text{N}$ chain ($\text{Ru}/\text{C}_5\text{N}$: 42/32%) (Fig. 2). In the case of the 2,4-pentadiynynitrile complex **4a'**, the HOMO ($\text{Ru}/\text{C}_5\text{N}$: 35/43%) and HOMO–1 ($\text{Ru}/\text{C}_5\text{N}$: 47/40%) are essentially derived from the anti-bonding combination of the orthogonal ligand π -systems with metal d-orbitals and are hence delocalised over the seven atom $\text{RuC}\equiv\text{CC}\equiv\text{CC}\equiv\text{N}$ chain (Fig. 3), whilst the LUMO has appreciable cyanocarbon π^* -character ($\text{Ru}/\text{C}_5\text{N}$: 8/64%). These general descriptions are very similar to those derived for closely related polyyne complexes,^{14,16} and highlight the electronic similarity in these ligand families.

Given this close electronic relationship between metal polyyne complexes $\text{Ru}\{\text{C}\equiv\text{C}\}_n\text{H}(\text{PR}_3)_2\text{Cp}$ and $\text{Ru}\{\text{C}\equiv\text{C}\}_n\text{C}\equiv\text{N}(\text{PR}_3)_2\text{Cp}$, it is somewhat surprising that calculations with the model radical cations $[\text{2a}']^+$ ($\nu(\text{C}\equiv\text{N})$ 2180 cm^{-1}), $[\text{3a}']^+$ ($\nu(\text{C}\equiv\text{CC}\equiv\text{N})$ 2091, 2288 cm^{-1}) and $[\text{4a}']^+$ ($\nu(\text{C}\equiv\text{CC}\equiv\text{CC}\equiv\text{N})$ 2055, 2183, 2288 cm^{-1}) reveal a significant degree of electronic and orbital relaxation in both $[\text{3a}']^+$ and $[\text{4a}']^+$ leading to heavily metal localised spin densities (SDs) in all cases (Fig. 4, see also Mulliken atomic SDs in Table S5[†]). The localised SDs contrast with the appreciable delocalisation of the α -SOMO

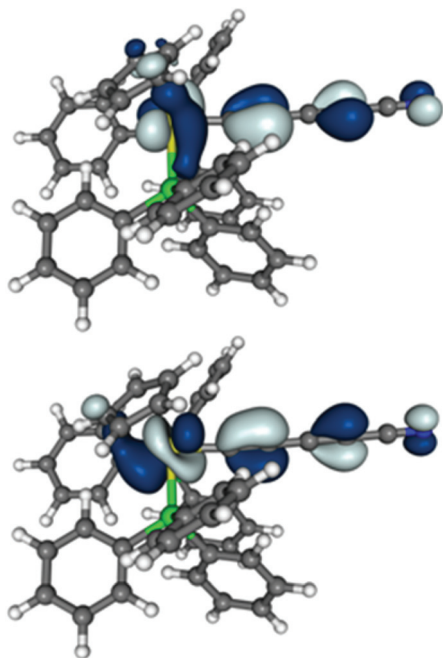


Fig. 3 Isosurface plots (± 0.04 ($e \text{ bohr}^{-3/2}$)) of the HOMO (top) and HOMO – 1 (bottom) of **4a'**.

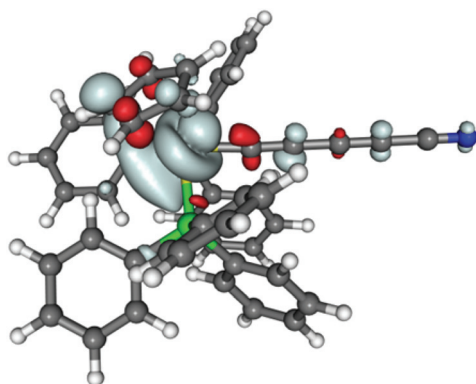


Fig. 4 Spin density isosurface plot (± 0.002 $e \text{ bohr}^{-3}$) of **[4a']⁺**.

over the C_3N - and C_5N -ligands, respectively. Such a localisation of the SD due to spin polarisation of the doubly occupied valence MO manifold is not uncommon for situations in which the SOMO is metal–ligand anti-bonding (cf. Fig. S3†).¹⁸ The spin density and orbital composition, together with the calculated vibrational frequencies and key bond parameters, support the description of **[2a'–4a']⁺** in terms of a formal Ru^{III} oxidation state. This observation contrasts the more ligand-based oxidation associated with polyyne chain complexes based on the same metal auxiliary.¹⁶

Conclusions

A simple synthetic route to the first examples of complexes bearing the 2,4-pentadiynynitrile ligand is reported. It

appears that despite the electronic similarities of closed shell/18-electron polyyne and cyanocarbon complexes, the cyanocarbon ligands in these ruthenium complexes are less able to support the unpaired electron than their all-carbon cousins. These electronic characteristics provide further opportunities to fine-tune the electronic properties of bimetallic ruthenium 'mixed-valence' complexes in a manner not available to the better known redox non-innocent all-carbon and carbon-rich systems.

Notes and references

†Crystal data for **4a**. $\text{C}_{46}\text{H}_{35}\text{NP}_2\text{Ru} \times (1.5\text{CH}_2\text{Cl}_2) \times (0.125\text{C}_6\text{H}_{14})$, $M = 902.92$, triclinic, $a = 8.8477(3)$, $b = 13.5114(5)$, $c = 18.6418(7)$ Å, $\alpha = 87.912(10)$, $\beta = 81.897(10)$, $\gamma = 72.388(10)^\circ$, $V = 2102.82(13)$ Å³, $T = 120$ K, space group $P\bar{1}$ (no. 2), $Z = 2$, $\mu(\text{MoK}\alpha) = 0.675$, 25 093 reflections measured, 10 610 unique ($R_{\text{int}} = 0.0467$) which were used in all calculations. The final wR_2 was 0.1293 (all data) and R_1 was 0.0473 ($7910 > 2\sigma(I)$). Crystal data for **4b**. $\text{C}_{41}\text{H}_{39}\text{NP}_2\text{Ru}$, $M = 708.74$, monoclinic, $a = 10.2903(2)$, $b = 22.7951(5)$, $c = 14.8498(3)$ Å, $\beta = 108.363(10)^\circ$, $V = 3305.92(12)$ Å³, $T = 120$ K, space group $P2_1/n$ (no. 14), $Z = 4$, $\mu(\text{MoK}\alpha) = 0.602$, 52 188 reflections measured, 8382 unique ($R_{\text{int}} = 0.0530$) which were used in all calculations. The final wR_2 was 0.1075 (all data) and R_1 was 0.0421 ($6925 > 2\sigma(I)$).

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